# MASS SPECTRA OF SOME BIVALENT TRANSITION-METAL ION CHELATES WITH PYRIDYLAZO PHENOLS AND NAPHTHOLS

#### D. BETTERIDGE and D. JOHN

Chemistry Department, University College, Swansea, Glamorgan, U.K.

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Summary—The mass spectra of 2- and 4-(2-pyridylazo)phenol, 2-(2-pyridylazo)-1- and 1-(2-pyridylazo)-2-naphthol and several chelates of these compounds with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) are discussed. Comparisons are made with the results of solution studies of complex formation of the same chelates.

PYRIDYLAZO PHENOLS, NAPHTHOLS AND RESORCINOL are now well established analytical reagents,<sup>1</sup> but the stoichiometry of several of the chelates is uncertain.<sup>2-4</sup> Mass spectrometry is, in principle, a good method for the establishment of stoichiometry and is a relatively unexplored approach.<sup>5</sup> Accordingly, we have obtained and examined the mass spectra of several chelates formed from these reagents and attempted to assess the value of mass spectrometry in the study of chelate chemistry.

#### EXPERIMENTAL

#### Reagents

Pyridylazo derivatives. 2-(2-Pyridylazo)phenol(o-PAP), 4-(2-pyridylazo)phenol(p-PAP), 2-(2-pyridylazo)-1-naphthol(o- $\alpha$ -PAN) and 4-(2-pyridylazo)-1-naphthol(p- $\alpha$ -PAN) were synthesised by reacting 2-hydrazinopyridine<sup>6</sup> with 1,2-benzoquinone, 1,4-benzoquinone, 1,2-naphthoquinone or 1,4-naphthoquinone respectively.<sup>7,8</sup> The quinones were either obtained commercially and purified before use or synthesized by published procedures. o- $\alpha$ -PAN was also prepared by the method described earlier.<sup>9</sup> 1-(2-Pyridylazo)-2-naphthol(o- $\beta$ -PAN) was obtained commercially. All the reagents were purified by recrystallization from 50% aqueous methanol or by sublimation. All were subjected to elemental analysis for carbon, hydrogen and nitrogen; the results were in agreement with the theoretical within the usual limits of accuracy. The mass spectra described below confirmed the purity of all but o- $\alpha$ -PAN. This impurity was found in samples prepared by different methods and in the chelates of o- $\alpha$ -PAN. It is possibly a tetrazo derivative, but further work is needed to verify this.

p- $\alpha$ -PAN could not be purified by these methods (it exploded rather than sublimed and gave tars on recrystallization) and consequently was not examined further.

Metal ion solutions. Solutions were prepared from analytical reagent grade salts and standardized by titration with EDTA.

Chelates. Equal volumes of equimolar  $(5.0 \times 10^{-3}M)$  solutions of metal ion in water and PAP or PAN in ethanol were mixed and a few drops of aqueous ammonia were added to ensure complete reaction. The solutions were heated and then allowed to stand whilst the chelate precipitated. This was then washed with water and dried *in vacuo*. This procedure generally yielded crystalline products.

#### Apparatus

Mass spectrometer. Spectra were obtained on solid samples with an A.E.I. MS9 double focussing mass spectrometer. One spectrum was run at a resolution of 15000 with heptacosafluorotributylamine as a reference; the rest were run at low resolution.

## **RESULTS AND DISCUSSION**

## Mass spectra of ligands

The spectrum of each ligand shows a well-defined parent peak and a similar fragmentation pattern (Figs. 1-4).







1-(2-Pyridylazo)phenol, (0-PAP). The spectrum of this ligand is typical and is discussed in detail to show the general pattern of fragmentation. The pathways of breakdown are summarized in Fig. 5. Steps accompanied by metastable peaks are known with certainty,<sup>10,11</sup> because they proceed according to the well-known relationship between parent,  $m_1$ , daughter,  $m_2$ , and metastable,  $m^*$ , *i.e.*,  $m^* = m_2^2/m_1$ . Other postulated steps are those that best fit the facts for reasons given below.



Numbers indicate value of m/e.

There is a peak at m/e 199<sup>†</sup> due to the parent ion, which then fragments in two ways: (i) by loss of nitrogen and (ii) by cleavage resulting in pyridine and phenolazo fragments.

(i) The loss of nitrogen is confirmed by a metastable peak at 171. It is probable that the mechanism is that indicated by



The recombination of the pyridine and phenol fragments with retention of the substitution patterns of the pyridine and phenol is suggested by the difference in fragmentation pattern of o- and p-isomers. The fragment corresponding to m/e 171 then breaks down by one of two routes, (*ia*) or (*ib*).

(*ia*) Loss of a hydrogen atom gives 170 (shown by a metastable peak at 169 on loss of another). The ratio of the abundance of 171 and 170 in the ligand and chelate

 $\dagger$  For convenience of discussion, units of m/e may be assumed and all fragments are named as if they did not carry any charge.

spectra show that it is the phenolic hydrogen that is lost. Comparison with p-PAP indicates that proximity of oxygen and nitrogen atoms may result in intermediates which facilitate the reaction, e.g.,



The next step is probably transfer of a proton from the pyridine to the phenolic ring with consequent cleavage of the bond between the rings. A metastable peak at 45.4 confirms the loss of carbon monoxide from the phenolic fragment 93 to give a five-membered ring. The steps of (*ia*) are



The minor peak at 142 may be due to the loss of carbon monoxide from 170.

(*ib*) There is an immediate rupture of the bond joining the rings without prior loss of hydrogen. The great abundance of 93 and 78 shows this to be a major pathway. Pyridine loses hydrogen cyanide to give  $C_4H_3$ .

(*ii*) The peak at 121 is probably due to a phenolazo fragment formed by cleavage of the azo-nitrogen pyridine bond of the parent. There is a loss of nitrogen (metastable 71.5) to give a peak at 93.

4-(2-Pyridylazo)phenol, (p-PAP). The spectrum is very similar to that of o-PAP and the fragmentation pattern can be interpreted in the same way. The only major difference is the ratio of peaks 171 and 170 commented upon above. An accurate mass measurement of peak 171 gave 171.0684. This confirms the formula  $C_{11}H_9NO$  and the elimination of nitrogen postulated above.

1-(2-Pyridylazo)-2-naphthol( $\circ$ - $\beta$ -PAN). The spectrum and mechanism of fragmentation are very similar to those of o-PAP, with naphthol being substituted for phenol. The postulated mechanism is shown in Fig. 6, which is self-explanatory. The differences noted are that the direct cleavage step (*ii*) is not noticeable and the ratio of peaks 221:220 compared with 171:170 of o-PAP is different and in favour of hydrogen loss.



FIG. 6.—Fragmentation pattern of 1-2(pyridylazo)-2-naphthol.



FIG. 8.—Mass histogram of chelate of manganese(II) and o-PAP. Temp. 380°C. **ww** = scale shortening.

2-(*Pyridylazo*)-2-naphthol,  $(0-\alpha$ -PAN). The spectrum (Fig. 4) is virtually identical with that of  $o-\beta$ -PAN, except for a large peak at 248 due to the parent minus hydrogen. The breakdown of this ion appears to follow a route analogous to (*ii*) of o-PAP.

#### Mass spectra of chelates

The spectra of the chelates examined (Figs. 7-13), with the exceptions of p-PAP compounds, are all similar. A parent peak is observed, but the peak due to the parent minus one ligand is stronger and very useful diagnostically.



Temp.  $380^{\circ}$ C.  $\cdots =$  scale shortening.

 $Zinc(0-PAP)_2$ . Zinc has 5 naturally occurring isotopes, with the following mass and abundance: 64(48.9%), 66(27.8%), 67(4.1%), 68(18.6%) and 70(0.6%). These make easy the identification of zinc-containing fragments in the spectrum. The major fragmentation pattern of the chelate is

$$ZnC_{22}H_{16}N_6O_2 \xrightarrow{-C_{11}H_8N_3O} ZnC_{11}H_8N_3O \xrightarrow{-C_6H_4N_2O} ZnC_5H_4N$$
  
464,462,460 266,264,262 146,144,142

with loss of one ligand followed by cleavage to give monopryidinezincate (146,144,142) and azophenolate (121). The ligand fragments follow the fragmentation pattern of the parent ligand. The large peak at 170 due to the ligand minus nitrogen and hydrogen, and the absence of a metastable peak at 169, show that a proton is lost during chelation; the parent peaks at 464, 462 and 460 demonstrate a stoichiometry of 1:2 metal:ligand. The spectra thus confirm the results of solution studies.

There are also minor peaks containing zinc at P - 28 and P - 121, where P is the parent peak m/e, corresponding to loss of nitrogen and azophenolate respectively.

Nickel(0-PAP)<sub>2</sub>. The doublet due to the most abundant isotopes of nickel, mass 58 and 60 and abundance 67.9% and 26.2%, enable nickel-containing fragments





to be readily identified. The spectrum is identical with that for  $Zn(o-PAP)_2$  when the difference in atomic weight is taken into account.

Manganese  $(o-PAP)_2$ . There is only one stable isotope of manganese, but when allowance is made for this and the difference in atomic weight the spectrum (Fig. 8) is almost identical with that of  $Zn(o-PAP)_2$ . The major difference is the appearance of a peak at 55, which if due to manganese-55 implies a change of oxidation state from II to I.

## Chelates formed between 0-a-PAN and zinc(II), nickel(II), manganese(II)

The spectra and fragmentation pattern of these chelates is completely analogous to that of the corresponding o-PAP chelate; that of Ni( $o-\alpha$ -PAN)<sub>2</sub> is shown (Fig. 9);

Copper  $(o-\alpha - PAN)_2$ . Copper has 2 stable isotopes of comparable abundance. 63 (69.1%) and 65 (30.9%). The most unusual feature of the spectrum is that there is no evidence of the expected doublet at M and M + 2, where M is the value of m/e for any ion containing copper-63 (Fig. 10). In all other respects the spectrum is in accord with that expected for copper-63. The possibility of the spectrum being a memory can be discounted because the spectrum shows the presence of  $o-\alpha$ -PAN and peaks at m/e > 249 which are not found in the other  $o-\alpha$ -PAN chelate spectra. The possibility of  $o-\alpha$ -PAN chelating with copper-63 preferentially is not in accord with general chemical experience or the results of solution studies on the system. Further, the spectrum we have obtained of copper acetylacetonate shows the expected isotopic pattern. This curious behaviour is being investigated in more detail.

Cobalt  $(0-\alpha-PAN)_2$ . We have not yet examined the solution chemistry of the reaction between cobalt(II) and  $o-\alpha$ -PAN, but the complex formed with  $o-\beta$ -PAN is unstable in air. The spectrum of  $Co(o-\alpha$ -PAN)<sub>2</sub> (Fig. 11) shows signs of decomposition not observed in the other spectra of  $o-\alpha$ -PAN chelates. There are several peaks unaccounted for and a large peak at 44 due to carbon dioxide. However, there is a parent ion peak at 555 confirming the 1:2 stoichiometry of the chelate, and a peak at 307 corresponding to the 1:1 chelate fragment, which suggests that the general fragmentation pattern is the same.

## Chelates formed between $0-\beta$ -PAN and zinc(II), manganese(II) and copper(II)

The spectra were very similar to those of the corresponding o-PAP and  $o-\alpha$ -PAN chelates; Fig. 12 is representative. One difference is that the parent peak is much smaller than it is in the spectra of o-PAP and  $o-\alpha$ -PAN chelates, where it is always a major peak and in one instance, is the base peak. The expected isotopic distribution is not found in the spectrum of the copper chelate, which behaves as though copper-63 were the only stable isotope of copper.

## Chelates between p-PAP and copper(II), nickel(II), cobalt(II) and iron(II)

p-PAP forms chelates with fewer metals than o-PAP and those that are formed have different solubilities. For example, the manganese chelate is not formed. These differences are explained by the facts that p-PAP is bidentate and that the ionizable proton is not at the centre of chelation. Thus, in the neutral chelate the ligand is probably in the quinonoid form and has adducts such as ammonia or water if the metal ion is in an octahedral configuration. Support for these deductions is found in the spectra, which are quite different from those discussed above.

The compounds are much less volatile and the spectra were obtained at the maximum temperature of the probe. Under these conditions the chelate falls apart and the major peaks in the spectrum are those observed for the free ligand ion. In the spectra of the copper, nickel and cobalt complexes there are several common minor peaks of great interest. The copper chelate (Fig. 13) is taken as typical; the figures are based on copper-63, again the only isotope appearing in the spectrum. The peak at 459, corresponding to  $Cu(p-PAP)_2$ , is observed, but in addition there are peaks at 439, 467 and 495. The latter could correspond to two water molecules or two ammonium ions. The spectra are not of sufficiently high resolution to decide unambiguously between these two. The peaks at 467 and 439 could correspond to the successive loss of nitrogen from 495, as in the minor pattern noted with o-PAP chelates. The spectra are too weak to show with certainty the metastable peaks accompanying these losses. The peaks between 495 and 198, the ligand ion, are common to all the spectra and therefore do not contain the metal ion. They must be peaks due to recombination of the ligand fragments of the type noted in the spectrum of bis[2-(4toluenesulphonamido]anilinecopper(II). It is not at all clear what the peaks actually correspond to but the following suggestions are in accordance with the observed mass differences: 311, loss of copper (63) and phenylazo (121) from parent; 339 and 246, loss of copper and one or two phenoxide (93) fragments from parent; 368, loss of copper and two water molecules from parent; recombination of the fragments remaining after these losses take place. Spectra of higher resolution are clearly required.

The spectrum of the cobalt complex does not show a parent ion peak at the expected value, but a peak at 246 suggests that it, like copper and nickel, has two co-ordinated water molecules.

The ion abundance, A, of the iron complex is given below. There are no peaks greater than that of the ligand ion, 198, but the fact that 199 is absent, *i.e.*, no protonated ligand, suggests that it conforms to the major fragmentation pattern of the other *p*-PAP chelates.

m/e	198	170	154	142	121	93	78	65	52	51	39	28
A, %	1.8	45•4	1.6	3.0	26.6	100	17.9	42.0	15.6	76·3	32.9	7.9

## Comparison of results from mass spectra and solution studies

Ligands. It is difficult to prepare pure PANs and sometimes difficult to prove the identity of the isomer isolated. Because of the large molecular and equivalent weight, elemental analysis and titration to determine the equivalent weight can give uncertain results. Mass spectrometry is very useful in these circumstances, provided the compound is volatile and stable enough to give a reasonable spectrum. It is especially valuable as a method of quality control during purification steps. There are small differences between the spectra of o- and p- compounds and these were sufficient to confirm that  $o-\alpha$ -PAN was incorrectly identified, as  $p-\alpha$ -PAN, when first examined as an analytical reagent.<sup>9</sup> Whether this evidence is preferable to that from infrared spectra is a matter of taste and experience; both methods give correct identification of the isomer, provided that there is a sufficient number of reliable reference compounds available, but neither explains the large difference in  $pK_{OH}$  between  $o-\alpha$ -PAN and  $o-\beta$ -PAN, which was the cause of the original misidentification.

Chelates of 0- $\alpha$ -PAN and 0- $\beta$ -PAN. In solution work it is generally found that

 $o-\alpha$ -PAN forms complexes more rapidly and with no ambiguity about the stoichiometry. We feel that it is better than  $o-\beta$ -PAN, which is nevertheless a very good analytical reagent. The mass spectra of  $o-\alpha$ -PAN chelates show a constant stoichiometry of 1:2, a large parent peak and no adducts such as ammonia or water. The spectra of  $o-\beta$ -PAN chelates are identical except for the smaller parent peak. From these results it is possible to deduce that the ligands are terdentate and that the complexes are stable, but that those of  $o-\alpha$ -PAN are the more stable.

The 1:2 stoichiometry of the copper(II) complex of  $o-\beta$ -PAN is most interesting, especially as the ratio of the peak of the 1:1 complex to the parent peak is not noticeably greater than that found for the other  $o-\beta$ -PAN chelates. The relative importance of the 1:1 and 1:2 complex in solution has been controversial from the time of the second measurement of the stability constants. The best assessment of the published work<sup>2</sup> is that the 1:1 complex is much more stable than the 1:2 complex and that in the latter  $o-\beta$ -PAN is bidentate. The recent crystallographic study by Fernando<sup>2</sup> would seem to have confirmed this view, but the mass spectrum suggests that the 1:2 complex is stable and the ligand is probably terdentate. The single crystal for the X-ray study was grown from a weakly acid solution whereas the compound was precipitated from alkaline solution in this study, but further work is needed to establish whether this is an important difference. The mass spectrum is singularly useful in determining the stoichiometry in this instance, because several workers have found it difficult to obtain a satisfactory elemental analysis of this chelate. The instability of the cobalt complexes and the complexity of their spectra have been noted above.

Chelates of o- and p-PAP. The mass spectra of o-PAP chelates support the conclusions of solution studies<sup>12-14</sup> and are so clear that they could usefully have preceded a solution study. The same cannot be said of the rather confusing spectra of p-PAP chelates. However there are points of interest that derive from the spectra. First, the spectra indicate the likelihood of mixed complexes being formed; this has not been inferred from the solution studies made to date. Second, the absence of adducts in the o-PAP spectra suggests that the ligand is terdentate, a view supported by solution and X-ray studies. Third, a correct assignment of the rearrangement fragments in the spectra of p-PAP chelates would be very valuable in deducing the correct stereochemical arrangement of the isomer; this type of information is not available from solution work and promises to be an area where mass spectrometry can contribute most to the understanding of chelates.

## Fragmentation patterns of mass spectra

In addition to the spectra discussed above, the mass spectra of chelates of acetylacetone,<sup>15</sup> benzoylacetone,<sup>16</sup> N,N'-ethylenebis-(benzoylpropylideneimine),<sup>17</sup> 8-hydroxyquinoline,<sup>18</sup> dimethylglyoxime<sup>19</sup> and 2-(4-toluenesulphonamido)aniline<sup>20</sup> have been recorded. Although it is already obvious that there are great differences in the fragmentation patterns of the different chelates, there are several points of similarity. Spectra which are clean and have a well-defined parent peak show evidence of fragmentation by loss of one ligand molecule as a first step. Spectra without a parent peak may exhibit rearrangement of ligand fragments,<sup>21</sup> which is useful in supplementing other studies but can be confusing initially (unless high resolution spectra can be obtained).

The stoichiometry suggested by the spectra must be interpreted with care, because

the peaks due to fragments of lower stoichiometry may be so much more intense than the parent that the parent peak is not detected. Thus the operator of the spectrometer must ensure that the part of the spectrum corresponding to the parent peak is scrupulously examined. We have also obtained the spectra of several acetylacetonates, which are in good agreement with those already published. There is no evidence of the hydrates or polynuclear chelates known from X-ray and solution work to exist.<sup>22</sup> Although absence of a peak may not be conclusive, presence of one is, and this may be extremely valuable in resolving a difficult problem of stoichiometry.

Shannon and Swan<sup>15</sup> have argued that the number of electrons in a fragment is important for stability and that stability of chelate fragments may be obtained by change in oxidation state. We have only found good evidence of such changes in the chelates of manganese; none in the chelates of cobalt and copper, which would be expected to behave in a similar manner. However, we cannot be dogmatic about this because the spectrum has so many peaks at the lower end that we were unable to determine the final fate of the metal ion. The calculated energies of the bonds in amine complexes<sup>23</sup> suggest that in a chelate the metal ligand bond may be the weakest, so the two postulated routes—loss of one or both ligands—may be the most likely, regardless of electron balance. Certainly it is true that a much greater difference exists between spectra of complexes of the same metal with different ligands than between complexes of the same ligand with different metals.

We have noted that the spectra of the copper chelates do not show the expected isotopic distribution. This is an observation which we are unable to explain, but if the phenomenon is more widespread it could cause confusion in spectral interpretation.

Acetylacetonates and chelates of o-PANs and o-PAP sublime and this may be a significant factor in their spectra being well defined and containing a parent peak. However useful spectra may be obtained with unstable or involatile compounds.

## CONCLUSION

Low resolution mass spectra of metal chelates of pyridylazophenols and naphthols can be easily obtained and are very valuable in interpreting or confirming the findings of other methods. There are limitations to the method and it is fundamentally a supplementary method. The 1:1 chelate fragments are very well defined and it may be possible to base analytical methods on them.

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Zusammenfassung—Die Massenspektren von 2- und 4-(2-Pyridylazo)phenol, 2-(2-Pyridylazo)-1- und 1-(2-Pyridylazo)-2-naphthol und mehreren Chelaten dieser Verbindungen mit Mangan(II), Kobalt(II), Nickel(II), Kupfer(II) und Zink(II) werden diskutiert. Vergleiche werden angestellt mit den Ergebnissen von Untersuchungen der Bildung derselben Chelate in Lösung.

**Résumé**—On discute des spectres de masse des 2- et 4-(2-pyridylazo) phénol, 2-(2-pyridylazo)1- et 1-(2-pyridylazo)2-naphtol et de plusieurs chélates de ces composés avec: manganèse(II), cobalt(II), nickel(II), cuivre(II) et zinc(II). On effectue des comparaisons avec les résultats d'études en solution de formation de complexe des mêmes chélates.

#### REFERENCES

1. R. G. Anderson and G. Nickless, Analyst, 1967, 92, 207.

2. D. Carter, Q. Fernando and Shun'ichiro Ooi, Chem. Commun., 1967, 1301.

- 3. W. J. Geary and F. Bottomley, Talanta, 1967, 14, 537.
- 4. L. Sommer and H. Novotná, *ibid.*, 1967, 14, 457.
- 5. H. Budzikiewicz, C. Djerassi and D. H. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, San Francisco, 1967.
- 6. R. G. Fargher and R. Furness, J. Chem. Soc., 1915, 107, 691.
- 7. F. M. Pollard, G. Nickless and R. G. Anderson, Talanta, 1966, 13, 735.
- 8. R. G. Anderson and G. Nickless, Proc. Soc. Anal. Chem., 1966, 3, 149.
- 9. D. Betteridge, P. K. Todd, Q. Fernando and H. Freiser, Anal. Chem., 1963, 35, 729.
- 10. K. Bieman, Mass Spectrometry, McGraw-Hill, New York, 1962.
- 11. F. N. McLafferty, Mass Spectrometry of Organic Ions, Academic Press, New York, 1963.
- 12. R. G. Anderson and G. Nickless, Anal. Chim. Acta, 1967, 39, 469.
- 13. Idem, Talanta, 1967, 14, 1221.
- 14. D. Betteridge and D. John, unpublished studies.
- 15. J. S. Shannon and J. M. Swan, Chem. Commun., 1965, 33.
- 16. C. G. MacDonald and J. S. Shannon, Australian J. Chem., 1966, 19, 1545.
- 17. S. H. H. Chaston, S. E. Livingstone, T. N. Lockyear and J. S. Shannon, ibid., 1965, 18, 1539
- 18. A. E. Jenkins, J. R. Majer and M. J. A. Reade, Talanta, 1967, 14, 1213.
- 19. A. E. Jenkins and J. R. Majer, ibid., 1967, 14, 777.
- 20. D. Betteridge and R. Rangaswamy, Anal. Chim. Acta, in press.
- 21. J. M. Williams and D. Betteridge, unpublished work.
- 22. G. J. Bullen, R. Mason and P. Pauling, Inorg. Chem., 1965, 4, 456.
- F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, pp. 46-51. Wiley, New York, 1958.